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## 21. ARTIFICIAL COBWEB: CHEMICAL AND PHYSICAL ANALYSIS

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### INTRODUCTION

During the war period in Croatia between 1991 and 1993 a new, unknown material was found at many locations in Croatia. This material appeared in the war operation zones, but also at distant places in the field, over broad areas. In appearance, it greatly resembles natural cobweb, but only from far away. On closer inspection, under the naked eye, and especially under a magnifying glass or a microscope, the differences become obvious. For example, in nature, there are no bundles of spider's cobweb having a diameter greater than 0.5 cm, as noticed at that time. A lot of other properties resemble those of natural cobweb, so the new material was nicknamed "artificial cobweb". This does not mean that "artificial spiders" attacked Croatia; no increase in spider population was noticed during the war, but the results of war operations, such as heavy mortar shelling and air raids, were strongly felt.

Artificial cobweb bundles were dispersed over kilometers of fields and meadows, stretched over rooftops, trees and bushes [1]. Such a matter having rather strange properties and shape was never previously observed in this part of Europe and therefore it caused an immediate public disturbance. However, no official or civil reports on its harmful activity were made, and therefore the disturbance faded soon. Since a similar appearance has not yet been reported in the scientific, technical or military literature, several civilian and government institutions, both inside and outside of Croatia, studied the properties of that matter. However, reports were rather rare and only preliminary [2-4].

Fig. 1. visualizes the morphology of artificial cobweb in the simplest way. Very fine, thin single-stranded fibers of different diameters are interwoven in bundles; occasionally, such bundles were found to be interwoven in very thick yarn. The matter stuck very easily to every other material (live, organic, inorganic and even metal) except to itself and it also floated on water.

Under the minute force of breeze or deliberate touch, the material extended extraordinarily. E.g., a part of a 5-cm long bundle could be stretched to a length of 20 m. The stretching was not a result of thinning of single fibers, but of their sliding and disentanglement. Therefore we speak about a virtual stretching.

### SAMPLING AND METHODS

The samples of artificial cobweb were collected both

- by civilians, in an inadequate manner
- by professionals, in sterile vessels.

In all cases it was noticed that after 10 to 20 days artificial cobweb disappeared (at least virtually). The investigation of falling water and snow-water was very useful and, for that purpose, the samples were collected by professionals, but in nonsterile vessels, as usual.

In Croatia, several different experimental techniques for studying cobweb were applied:

- low- and high-magnification light microscopy  
(up and down illumination, polarized light)
- electron microscopy (SEM, TEM)
- Raman and micro-Raman spectroscopy

- Fourier-transform infrared spectroscopy (FTIR)
- X-ray diffraction
- C, H, N analysis
- proton induced X-ray emission (PIXE).

However, the most successful were light microscopy, infrared spectroscopy and electron microscopy. The samples were studied:

- as intact, nontreated,
- in water solutions, in other organic solvents,
- sometimes wet, or after drying,
- stained, or C or Au deposited.

The samples were also expedited by private, scientific and official channels to a number of institutions in different countries. As far as we know, the results of foreign analyses were, in general, only a confirmation of our cognition, unfortunately, without any new ideas.

During this investigation our laboratories noted numerous results (records by photo-, video- and digital camera technique, or by FTIR spectrometer) characterizing cobweb material that was delivered in the atmosphere above Croatia in respectable amounts. Among them only a restricted number is presented here.

## RESULTS AND DISCUSSION

### Light microscopy

Fig. 2. shows "fresh" bundles of artificial cobweb in free space under polarized light (illumination from below, crossed polarizer and analyzer, long-working distance objective, 50x). This is one of the oldest video records, where we noticed that single-fiber diameters range between some 0.5  $\mu\text{m}$  and 10  $\mu\text{m}$ . Under the same microscope in the Mol. Phys. Lab. it was noticed in 1992 that artificial cobweb partially dissolved in essential liquids of plants and animals, and that lung tissue rotted when came into *in vitro* contact with cobweb matter.

Also, by the end of 1992 the atmosphere above Croatia was full of dust, especially that of organic origin[4]. The investigation of snow-water, its floats and precipitates proved to be particularly useful for this research. For that purpose, the first snow surface was removed, and then, "clean" snow was collected letting it to melt in a closed vessel for floated and suspended impurities. Fig. 3. presents an artificial cobweb tuft obtained in that manner. A piece of artificial cobweb yarn collected another thick fiber of different origin. The total sample length exceeded by about 3 mm. Perhaps, this sample was crucial for the recognition of gelatinous substance and microorganisms. Namely, in order to quicken the snow melting, the sample was slightly warmed for a short time. Under higher magnification (Fig. 4.), one can observe different microorganisms (mainly bacteria), especially close to the fiber ends of the same sample. Microorganisms can also be well observed at the border of dried water droplet (Fig. 5.). Higher concentration of microorganisms at the droplet boundary and close to the fiber ends could be a direct consequence of a drying process. Water that originally, *in vitro*, covers the entire sample retreats from the sample top (little hill) towards the drop edges, rinsing the sample and carrying microorganisms towards the fiber ends and the droplet boundary. Probably, the surface tension plays an important role in this process. Very often the entire food chain of different microorganisms, like coccoides, anthracoides, actinomycetes and yeasts, was developed at such places that are rich in food necessary for their survival.

### Electron microscopy

Very many accretions to single fibers were observed using scanning electron microscopy (Fig. 6.). However, it is still an open question whether these attachments are formed by dust particles from the atmosphere, by microorganisms arrived from the atmosphere, or by microorganisms developed in the yarn. SEM also confirmed the results of light microscopy on the existence of gelatinous substance that holds single fibers interwoven in bundles. Warm water (applied for a short time) makes gelatinous substance less viscous. Upon cooling and drying, gelatinous mass appears in the form of "rags" and "fringes", as presented in Fig. 7. Scanning and transmission electron microscopy were also used to determine a single fiber's thickness. The smallest diameters detected by these two methods ranged between 0.1  $\mu\text{m}$  and 1  $\mu\text{m}$ . For the observation of thicker single fibers, light microscopy was more useful.

### Infrared spectroscopy

Fig. 8. shows characteristic IR bands of artificial cobweb. The untreated sample was pressed into a KBr pellet after an especially cautious milling. To obtain a good spectral quality, it was necessary to repeat the milling and pressing procedures several times. Positions of all important bands are given just for easier recognition of that matter for the case of its appearance in some other war or terrorist occasions. In Fig. 9. we compare the spectra of several samples collected at different locations at different times during the war. Only slight differences of relative intensities can be seen in the region of

- O-H stretching of water
- C-H stretching of aliphatic carbohydrates
- sharp band at 1390  $\text{cm}^{-1}$ .

The overall spectral contour was always the same.

Comparison of the FTIR spectra of many materials revealed some that are spectroscopically very similar. Among them are man-made polymers such as nylons (especially 6/6), but here we compare only some of the spectra recorded for samples prepared in our laboratories (Fig. 10.) Obviously, materials such as polysaccharides, proteins and microorganisms could be mixed into the artificial cobweb and hardly distinguished from the basic substance by any method. In other words, the masking technique has been developed here almost perfectly.

### CONCLUSION

Here we list only the most important chemical and physical properties of the foreign matter that was "delivered" in the Croatian atmosphere in respectable amounts:

- man-made product, organic fibrous matter
- composite structure of at least two materials
- hierarchic morphology similar to tendon
- interaction with essential liquids of plants and animals
- covering material: gelatinous (collagen, agar-agar,?)
- core, carrying material: much higher strength
- always followed by microorganisms
- complicated structure and morphology are very suitable for biochemical warfare and terrorism.

Why do we consider this part of the war affairs so dangerous and worthy of the present and future investigations? During the war an expensive *full-scale biological experiment* was conducted from outside, but in the atmosphere above Croatia. Finally, Fig. 11. shows a photograph of one sample which was delivered in the Croatian atmosphere ten

years ago, but this photograph was taken only ten days before the CBMTS congress. Ten years after the war, artificial cobweb does not disappear under laboratory conditions. The disappearance of the artificial cobweb, observed in the field, is an apparent illusion and means only dissemination of it from abroad. Because of possible consequences to public health, we invite all peaceful and independent scientists as well as all people of good will to disclose the true nature and aim of this substance.

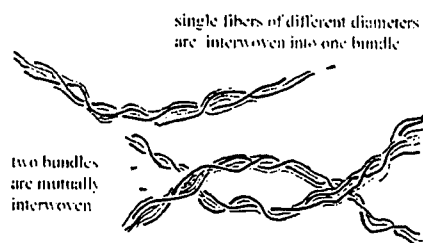
**KEYWORDS:**

cobweb, biochemical warfare, composite structure

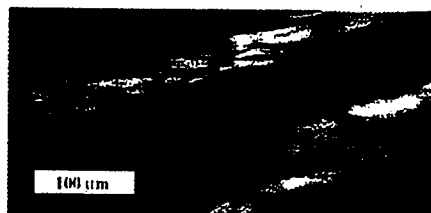
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2. G. B. Carter: Cobwebs in Chemical and Biological Warfare. ASA Newsletter **93-1** (1993) 6-7
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4. K. Furić, M. Ivanda, J. Kučar Kopic and V. Mohaček: Remarkable increase of organic particles in the atmosphere above Croatia. Spectrochim. Acta **50A** (1994) 449-462.

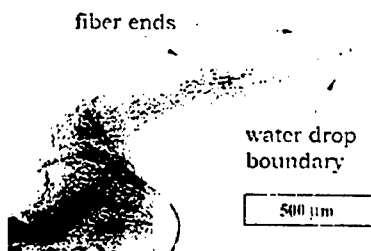
**FIGURES AND TABLES**



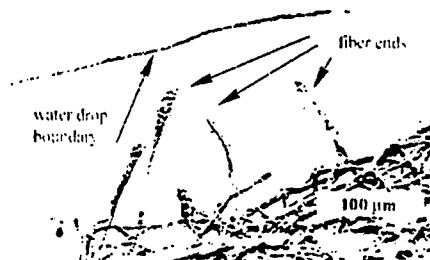
**Fig. 1.** Simplified drawing of artificial cobweb (yarn)



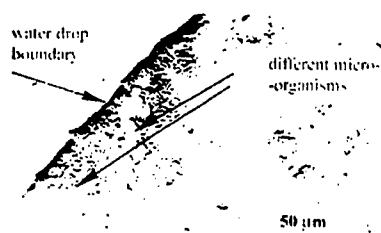
**Fig. 2.** Micrograph of two "fresh" bundles in polarized light



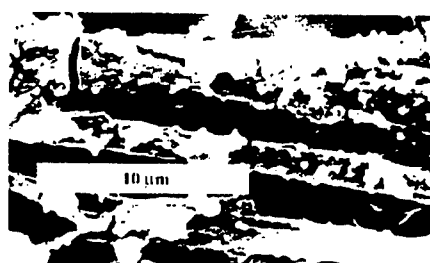
**Fig. 3.** Cobweb tuft from snow-water



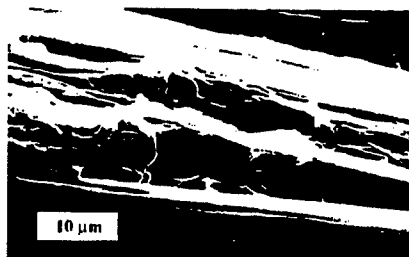
**Fig. 4.** Microorganisms appear close to fiber ends



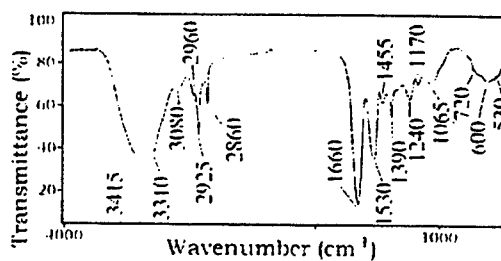
**Fig. 5.** Food chain of microorganisms is often



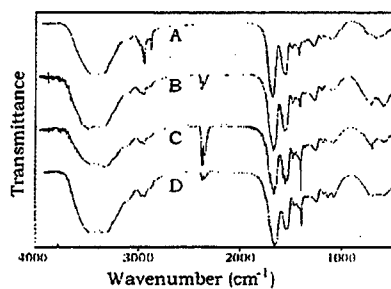
**Fig. 6.** SEM, agglutinated particles on cobweb yarn



**Fig. 7.** SEM, cobweb after 30' warming in water

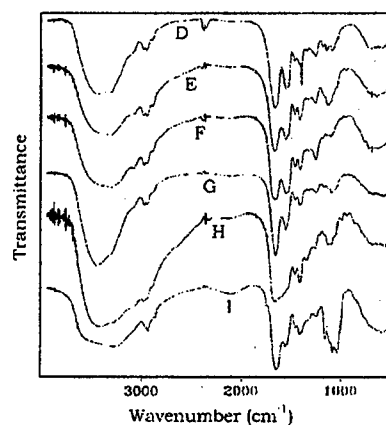


**Fig. 8.** Characteristic IR bands of artificial cobweb

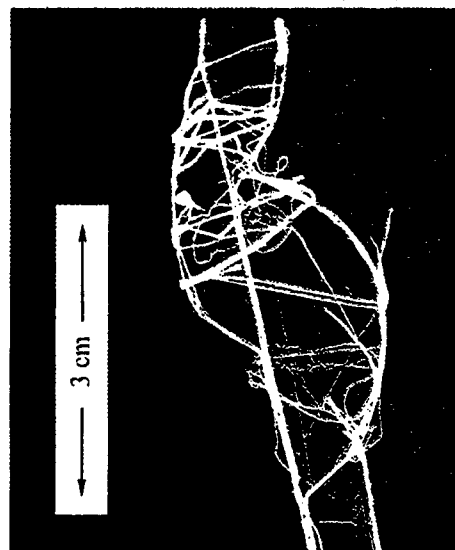


**Fig. 9.** Spectral comparison of different cobweb samples

A-D cobweb	G <i>Bacillus</i> sp.
E collagenase	H agar-agar
F crystalline	I yeast+bact.



**Fig. 10.** Some spectroscopically (FTIR) similar materials



**Fig. 11.** Ten years later artificial cobweb does not disappear in laboratory conditions